

# The efficiency of the Heterogeneous Photo-Fenton Process for Methyl Orange Degradation: A Review

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**Abstract:** Methyl orange dye is an organic pollutant often found in textile industry waste and harms the environment due to its nature, which makes it difficult to decompose naturally. One method that has attracted attention in its processing is the Photo-Fenton process, which utilizes hydroxyl radicals ( $\bullet\text{OH}$ ) as powerful degradation agents. This article summarizes recent developments in applying heterogeneous Photo-Fenton to Methyl Orange degradation, focusing on degradation efficiency, factors influencing reactions, and degradation pathways. This study discusses the influence of reaction parameters such as initial pH,  $\text{H}_2\text{O}_2$  concentration, catalyst concentration and light intensity on the degradation rate. In addition, various types of heterogeneous catalysts, including metal oxide-based and ferrous composites, were analyzed based on their effectiveness and stability in the Photo-Fenton system. The Methyl Orange degradation pathway is proposed based on an intermediate product identified in previous studies, suggesting that the reaction proceeds through a gradual oxidation mechanism until simpler and more environmentally friendly compounds are formed. The results of this study show that the heterogeneous Photo-Fenton system provides advantages over homogeneous systems, especially in increasing degradation efficiency and prolonging the catalyst reactivity cycle. The use of heterogeneous catalysts allows for the formation of larger numbers of active species, thus accelerating the breaking of the Methyl Orange structure. In addition, further research is needed to improve the stability of the catalyst, optimize reaction conditions, and evaluate its potential application on an industrial scale. This study will be a reference for developing a more efficient and sustainable Photo-Fenton-based waste treatment method.

**Keywords:** Degradation; Heterogeneous Catalyst; Methyl Orange; Photo-Fenton.

## Introduction

Environmental pollution due to textile industry waste and dyes has become a global concern because of the content of synthetic dyes that are difficult to decompose, one of which is Methyl Orange (MO), which belongs to the group of azo dyes and is widely used in the textile, paper, plastic, and laboratory industries as an indicator of pH [1-3]. Its stable chemical structure with azo bonds ( $-\text{N}=\text{N}-$ ) makes it difficult to degrade naturally, so its presence in wastewater can pollute the environment, change the color of water, reduce sunlight penetration, and inhibit the photosynthesis of aquatic organisms such as phytoplankton [4]. In addition, MO is toxic to aquatic organisms, can potentially cause mutagenic and carcinogenic effects, and can enter the food chain, harming human health [5]. Therefore, effective and environmentally friendly waste treatment methods are needed to remove MO before it is discharged into the environment to prevent negative impacts on ecosystems and human health [6].

The Photo-Fenton method is one of the Advanced Oxidation process (AOP) techniques proven effective in decomposing persistent organic compounds such as Methyl Orange [7]. This process relies on a combination of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  as the main oxidizing agent, with the help of light (UV or visible light) to improve degradation efficiency by forming highly reactive hydroxyl radicals ( $\bullet\text{OH}$ ).  $\bullet\text{OH}$  radicals have a high oxidation potential ( $E^0 = 2.8 \text{ V}$ ). Hence, they can break azo bonds in the MO structure, converting

them into simple compounds that are more easily degradable into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  [8]. The main advantage of this method is its ability to effectively remove color and lower MO toxicity without producing harmful secondary waste [9].

The homogeneous Photo-Fenton process uses  $\text{Fe}^{2+}$  in solution and has long been used in waste treatment. However, this method has some limitations, especially related to the precipitation of  $\text{Fe}^{3+}$  in neutral to alkaline pH, which reduces the efficiency of the reaction and causes difficulties in separating iron from wastewater [10]. Alternatively, heterogeneous Photo-Fenton offers several advantages over homogeneous methods. This catalyst not only prevents the loss of Fe in the solution but can also be reused, making it more environmentally friendly and economical. In addition, some heterogeneous catalysts have additional photocatalytic properties, which allow them to absorb visible light and accelerate the regeneration of  $\text{Fe}^{2+}$  from  $\text{Fe}^{3+}$ , thereby increasing the production of  $\bullet\text{OH}$  radicals [11]. Thus, the heterogeneous Photo-Fenton process offers a more stable, efficient, and sustainable solution in treating waste containing Methyl Orange compared to homogeneous methods.

## Research Methods

This literature review is compiled based on the Systematic Literature Review (SLR) method by following the guidelines of Preferred Reporting Items for Systematic Review and Meta-Analyses (PRISMA). Article searches

## How to Cite:

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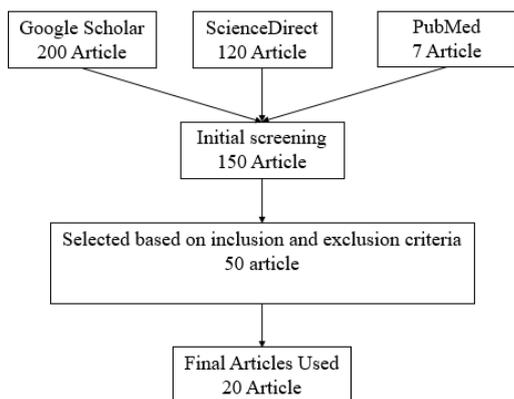
were conducted through scientific databases such as PubMed, Google Scholar, and ScienceDirect using the keywords "Photo-Fenton", "Heterogeneous Catalyst", and "Methyl Orange Degradation". The articles found were filtered based on inclusion and exclusion criteria to ensure relevance to the research objectives. Inclusion criteria included articles discussing using the Foto-Fenton heterogeneous method, reporting the degradation efficiency of Methyl Orange, and using heterogeneous catalyst characterization in the study. Articles that use the homogeneous Fenton method, without degradation efficiency tests, or do not list the experimental parameters are excluded from the review. The Population, Intervention, Control, and Outcome (PICO) framework is used to select articles that are in accordance with the research objectives. The selected articles were further analyzed to evaluate the effectiveness of the Foto-Fenton heterogeneous method against Methyl Orange degradation and compare the efficiency of different heterogeneous catalysts.

**Table 1.** PICO Framework

	PICO
Population (P)	Wastewater containing Methyl Orange dye
Intervention (I)	Heterogeneous Photo-Fenton method using metal-based catalysts
Comparison (C)	Catalyst-free systems or other methods such as Fenton homogeneous
Outcome (O)	Methyl Orange degradation efficiency based on degradation percent and final product characterization

**Table 2.** Inclusion and Exclusion Criteria

Inclusion	Exclusion
Photo-Fenton heterogeneous	Fenton homogeneous or non-Fenton method
Degradation efficiency, catalyst type, experimental conditions	No mention of the efficiency or parameters of the experiment
Methyl Orange	Other dyes or complex mixtures
Last 10 years	More than 10 years old or not fully available



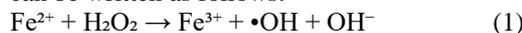
**Figure 1.** Research article selection flow

## Results and Discussion

### Photo-Fenton

The Photo-Fenton process is an effective advanced oxidation method for degrading complex organic compounds [7]. The main mechanism of this process is the formation of highly reactive hydroxyl radicals ( $\bullet\text{OH}$ ) through a reaction between hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), iron ions ( $\text{Fe}^{2+}$ ), and exposure to ultraviolet (UV) light [11]. These hydroxyl radicals can break dye molecules into simpler, less harmful compounds [12].

In detail, the reaction of hydroxyl radical formation can be written as follows:



The Photo-Fenton process is an effective photodegradation technique to decompose organic pollutants in wastewater. In a homogeneous system,  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  produce hydroxyl radicals ( $\bullet\text{OH}$ ) as strong oxidants, with UV light aiding in the regeneration of  $\text{Fe}^{2+}$  through photoreduction. Heterogeneous systems use metal catalysts such as  $\text{CuFe}_2\text{O}_4$  or  $\text{Fe}_2\text{O}_3$ , which, when irradiated by UV, form electron-hole pairs ( $e^-/h^+$ ), producing  $\bullet\text{OH}$  for pollutant degradation (Fig.2) [13]. The advantage of heterogeneous systems is that the catalysts can be separated and reused, making them more environmentally friendly and economical [14]. Given these benefits, the Photo-Fenton method emerges as an innovative approach to organic compound degradation, surpassing conventional methods such as the Fenton process and photocatalysis. Research findings further support this advantage, demonstrating that Photo-Fenton achieves superior efficiency in breaking down Methyl Orange, as summarized in Table 3.

**Table 3.** Efficiency of various methods in Methyl Orange degradation

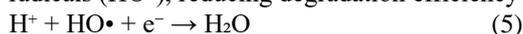
Method	Methyl Orange	Degradation Efficiency / Reaction time	Ref
Fenton	20 mg/L	87% / 120 min	[15]
Photocatalysis	10 mg/L	89% / 120 min	[16]
Photo-Fenton	10 mg/L	96% / 120 min	[16]

Photo-Fenton showed the highest degradation efficiency compared to other methods, with 96% degradation of methyl orange (10 mg/L) within 120 minutes. This advantage comes from the synergy of the Fenton reaction and light exposure, which accelerates the formation of hydroxyl radicals ( $\bullet\text{OH}$ ) as powerful oxidants. Light also aids in the regeneration of  $\text{Fe}^{2+}$  from  $\text{Fe}^{3+}$ , ensuring that the oxidation process continues to take place effectively and with high efficiency [16].

### Influential Reaction Parameters

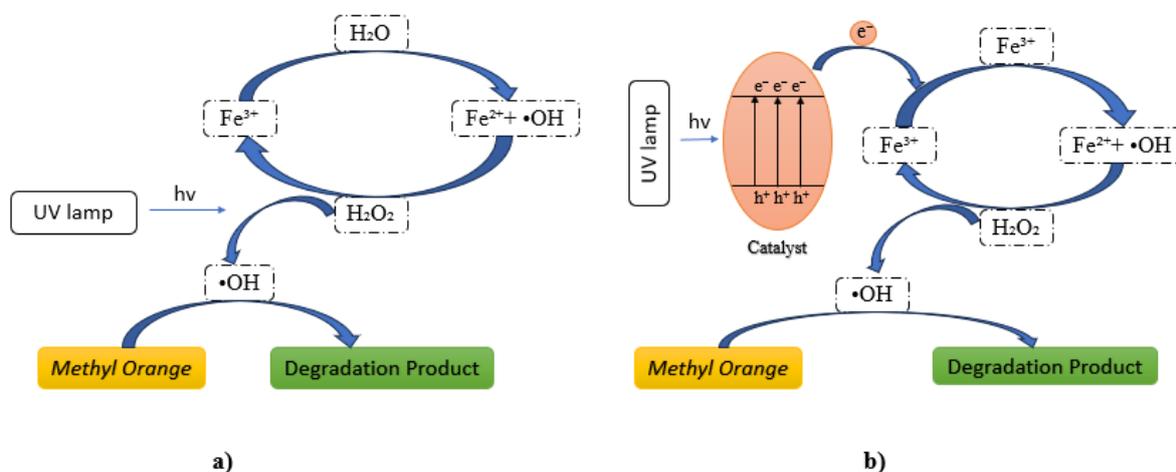
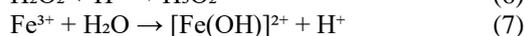
The effect of solution pH on Methyl Orange (MO) degradation shows significant variation in degradation efficiency in various catalytic systems. Acidic conditions with a pH of around 3–5 are considered optimal, as in this range MO tends to be in the form of zwitterion with

electrostatic interactions that favor degradation [17]. However, at pH below 3, excess H<sup>+</sup> ions capture hydroxyl radicals (HO•), reducing degradation efficiency [18]



In addition, previous studies have confirmed that with increasing pH, the number of HO• radicals formed from the decomposition of H<sub>2</sub>O<sub>2</sub> decreases significantly [19], and H<sub>2</sub>O<sub>2</sub> undergoes solvation in an acidic medium (pH ≤ 2.5),

forming an oxonium ion (H<sub>3</sub>O<sub>2</sub><sup>+</sup>) that increases the stability of hydrogen peroxide, thereby limiting the production of hydroxyl radicals [20]. At higher pH (above 7), hydrolysis of iron ions produces hydroxide deposits that decrease catalyst activity



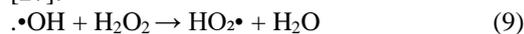
**Figure 2.** Photo-Fenton Process a) Homogeneous system b) Heterogeneous system

Catalyst concentration significantly influences the efficiency of organic compound degradation in the Photo-Fenton process. Catalysts generate holes (h<sup>+</sup>), superoxide radicals (•O<sub>2</sub><sup>-</sup>), and hydroxyl radicals (•OH), which drive oxidation reactions [21]. Increasing catalyst doses generally enhance adsorption and degradation, but particle agglomeration and increased turbidity hinder light transmission beyond the optimal dose, reducing reaction efficiency [22,23]. Studies show that Increasing the dose of Fe-MMT-1.5 from 0 to 2 gL<sup>-1</sup> increases the efficiency of Methyl Orange (MO) decolorization due to the more active sites of iron, which accelerates the decomposition of H<sub>2</sub>O<sub>2</sub> to HO• radicals. The highest efficiency (59.9%) was achieved at a dose of 2 gL<sup>-1</sup>. However, increasing the dose to 3 gL<sup>-1</sup> reduced the efficiency to 56.2% due to the scavenging effect by excess iron and the increased side reaction of Fe<sup>3+</sup> with H<sub>2</sub>O<sub>2</sub> which produces HO<sub>2</sub>•, which is less reactive than HO<sub>2</sub> in the oxidation of organic compounds [24].



The effect of hydrogen peroxide concentration on the degradation of Methyl Orange (MO) in the Photo-Fenton process is highly dependent on the balance between the production and consumption of hydroxyl radicals (•OH), which act as the main oxidant [25]. The hydroxyl radicals formed have a high redox potential (+2.8 V) and are highly reactive in oxidizing MO into simpler degradation products. However, with an increase in H<sub>2</sub>O<sub>2</sub> concentration, there is an increase in the number of hydroxyl radicals that can accelerate the degradation of MO in the early stages of the reaction. Studies show that in the 12–64 mM range, degradation efficiency increases to 90% within 60 minutes at an optimal concentration of 24 mM [26]. However, when the

concentration of H<sub>2</sub>O<sub>2</sub> exceeds the optimal value, a scavenging effect causes a decrease in degradation efficiency. This is due to the overconsumption of hydroxyl radicals in a side reaction with H<sub>2</sub>O<sub>2</sub>, which produces hydroperoxyl radicals (HO<sub>2</sub>•) with lower oxidation potential [27].



Light intensity is an important factor affecting the efficiency of dye degradation in the Photo-Fenton process [28]. In general, an increase in light intensity correlates with an increase in the number of photons available per unit area, which plays a role in catalyst excitation and the formation of electron-hole pairs [29,30]. In addition, experiments with variations in light intensity from 993 to 5560 lux showed that the decolorization efficiency increased from ~74% to ~93% as the intensity increased from 993 to 1620 lux [31]. However, too high light intensity can decrease degradation efficiency due to faster electron-hole pair recombination or the system's inability to utilize light energy optimally [32,33].

### Types of Heterogeneous Catalysts Used

Iron oxide catalysts are among the most common heterogeneous catalysts used in the Photo-Fenton process. Iron oxide also has advantages in terms of chemical stability and can be modified in the form of nanoparticles to increase its surface area and catalytic activity [34]. The pH of the solution strongly influences the use of iron oxide in Photo-Fenton, as the stability of Fe<sup>2+</sup> ions in aqueous solutions may change depending on the acidity conditions of the medium.

**Table 4.** Performance of iron oxide catalysts in degradation processes

Types of Catalysts	[MO]	pH	[H <sub>2</sub> O <sub>2</sub> ]	[Catalyst]	Light	Degradation Efficiency	Reaction time	Ref.
Fe <sub>3</sub> O <sub>4</sub>	-	3.5	-	-	UV (ultraviolet)	98.3 %	110 min	[35]
α-Fe <sub>2</sub> O <sub>3</sub> Nanoparticles	100 mg/L	3.0	5 mM	3 g/L	UV-vis	99.55 %	4 min	[36]
Urchin-like α-Fe <sub>2</sub> O <sub>3</sub>	2.5 mg/L	3.0	0.3 mM	-	UV- C lamp	76.5 %	120 min	[37]
Fe <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub>	-	3.0	0.3 mM	-	UV- C lamp	98 %	60 min	[38]
Silica Gel/Fe <sub>2</sub> O <sub>3</sub>	250 mg/L	2.0	8 mM	10 g/L	UV- C lamp	91 %	120 min	[39]

**Table 5.** Performance of Iron-based composite catalysts in degradation processes

Types of Catalysts	[MO]	pH	[H <sub>2</sub> O <sub>2</sub> ]	[Catalyst]	Light	Degradation Efficiency	Reaction time	Ref.
Ilmenite Sands	10 mg/L	2.5	1 mM	2 g/L	UV-B lamp	100 %	45 min	[40]
CuFe <sub>2</sub> O <sub>4</sub> /biochar composite	10 mg/L	3.0	10 mM	1 g/L	Visible light	98 %	60 min	[41]
Fe-sand	0.1 g/L	3.0	20 mM	-	UV (ultraviolet)	100 %	60 min	[42]
MnFe <sub>2</sub> O <sub>4</sub> @CPB Composite	10 mg/L	3.0	1 mM	0.25 g/L	Visible light	99.5 %	150 min	[43]
Fe- Laponite @diatomite	50 mg/L	3.43	20 mM	-	UV (ultraviolet)	99 %	240 min	[44]

**Table 6.** Performance of Iron-based semiconductors in degradation processes

Types of Catalysts	[MO]	pH	[H <sub>2</sub> O <sub>2</sub> ]	[Catalyst]	Light	Degradasi Efficiency	Reaction time	Ref.
TiO <sub>2</sub> /V <sub>2</sub> O <sub>5</sub>	10 mg/L	6.8	10 mM	-	UV (Ultraviolet)	90 %	180 min	[45]
Fe <sub>3</sub> O <sub>4</sub> /g-C <sub>3</sub> N <sub>4</sub>	10 mg/L	4.0	80 mM	5 g/L	UV-Visible light	96 %	120 min	[16]
α- Fe <sub>2</sub> O <sub>3</sub> /Bi <sub>2</sub> WO <sub>6</sub>	-	5.5	3 mM	-	UV-vis	85% (vis) 100% (UV)	60 min	[46]
NiFe <sub>2</sub> O <sub>4</sub> /CoMoS <sub>4</sub>	10 mg/L	2.0	2 mM	3 g/L	Visible light	99 %	60 min	[47]
Cu <sub>2</sub> ZnSnS <sub>4</sub> /ZnFe <sub>2</sub> O <sub>4</sub>	10 mg/L	6.0	10 mM	0.5 g/L	Visible light	91 %	120 min	[48]

Iron-based composite catalysts are a type of catalyst consisting of iron oxide combined with other supporting materials such as carbon, zeolite, or silica to increase their catalytic activity and stability [49]. One of the major drawbacks of iron oxide catalysts is their tendency to leaching or excessive release of Fe<sup>2+</sup> ions into the solution, which can lead to secondary contamination [50]. To address this, graphene oxide (GO) is often used as catalyst support to improve stability and adsorption capacity. For example, Fe<sub>3</sub>O<sub>4</sub>/GO can improve the degradation efficiency of Methyl Orange due to the combination of the catalytic effects of Fe<sub>3</sub>O<sub>4</sub> and the conductive properties and high surface area of graphene oxide [51]. Iron-based semiconductors are a type of catalyst that can absorb light and harness photon energy to produce electron-hole pairs (e<sup>-</sup>/h<sup>+</sup>) that can accelerate Photo-Fenton reactions [52]. One example of an iron-based semiconductor often used is hematite (α-Fe<sub>2</sub>O<sub>3</sub>), which has a band gap of about 2.1 eV, allowing the absorption of visible light to increase the production of hydroxyl radicals [53].

Although heterogeneous catalysts offer advantages over homogeneous systems, the main challenges still faced are catalyst stability and the risk of iron leaching, i.e. the

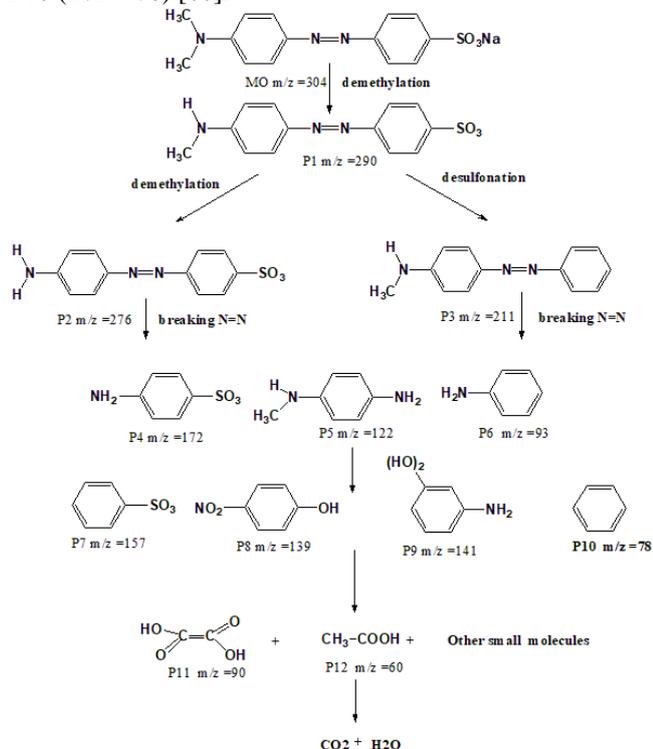
release of Fe<sup>3+</sup> ions into the solution during the reaction. Iron leaching not only leads to a decrease in degradation efficiency in the long term but also has the potential to cause secondary pollution if the dissolved Fe ions are not properly managed[54,55]. To address this problem, various strategies have been developed, such as the immobilization of Fe in supporting materials (activated carbon, zeolite, or silica), doping with other metals (e.g. Cu or Zn), as well as the use of composite structures to improve catalyst stability and slow down the release of Fe ions.

The studies showed that the GO Modification in nZVI/O-GO-1:1 increased stability and decreased the release of iron ions, making it superior to pure nZVI. The data showed that Fe<sup>2+</sup> in nZVI decreased drastically after 60 minutes, while nZVI/O-GO-1:1 remained stable for up to 180 minutes, signalling a slower and controlled iron release. GO's wrinkled structure helps capture iron ions, prevents overoxidation, and increases its recyclability [56]. Research on MILs(Fe) in Fenton-like catalysis shows that pH influences catalyst activity and stability. At pH 3, the initial activity is high but rapidly declines due to active site deactivation and structural decomposition. In weakly acidic

conditions, the initial activity is lower but more stable with minimal Fe leaching, while in neutral conditions, stability increases, but catalytic activity decreases. Therefore, balancing activity and stability is key to optimizing Fe-based catalysts for wastewater treatment [57].

### Degradation products and degradation pathways of Methyl Orange

The degradation products and degradation pathways of Methyl Orange (MO) in the oxidation process, such as those analyzed using LC-MS [58], GC-MS [42] and HRMS [43], show that the attack of hydroxyl radicals precedes degradation ( $\bullet\text{OH}$ ) on the azo group ( $-\text{N}=\text{N}-$ ) connecting the two aromatic rings. This process produces a variety of intermediate compounds, including dimethylaniline and sodium benzenesulfonate. In the initial stage, MO with  $m/z = 304$  loses  $\text{Na}^+$  ions due to dissolution in water [59].  $\bullet\text{OH}$  attack on the methyl nitrogen group of tertiary amines results in P1 ( $m/z = 290$ ), which then undergoes the elimination of the methyl and sulfonic acid groups, forming P2 ( $m/z = 276$ ) and P3 ( $m/z = 211$ ). Furthermore, the disconnection of azo groups results in P4 ( $m/z = 172$ ), P5 ( $m/z = 122$ ), and P6 ( $m/z = 93$ ), which then undergo further transformation through the release of  $-\text{SO}_3$  groups and the addition of hydroxyl groups, forming P7 ( $m/z = 157$ ), P8 ( $m/z = 139$ ), P9 ( $m/z = 141$ ), and P10 ( $m/z = 78$ ) [60].



**Figure 3.** Methyl Orange degradation path [58]

The oxidation process continues with the breaking of the C-N bond between the methyl group and the nitrogen atom, resulting in the replacement of the methyl group with a proton and the resulting P11 ( $m/z = 290$ ) as well as P12 ( $m/z = 276$ ), which indicates the loss of one or two methyl groups at MO [16]. Breaking benzene rings further produces intermediate compounds such as benzene ( $m/z = 78$ ) and phenol ( $m/z = 94$ ). In mass spectrometry analysis after 20 minutes of irradiation, peaks of  $m/z$  were detected at 158 and 93, which were identified as benzenesulfonic acid and

aniline. After 50 minutes, the peak intensity of the intermediate compound decreases, indicating further degradation. Eventually, after 60 minutes of irradiation, the degradation product undergoes complete disconnection, producing  $\text{CO}_2$  ( $m/z = 44$ ) and  $\text{H}_2\text{O}$ , indicating that MO has undergone complete degradation in the oxidation system used.

### Conclusion

This literature review concludes that the heterogeneous Photo-Fenton process is an effective and promising method for degrading Methyl Orange (MO), offering advantages in catalyst stability and ease of separation compared to homogeneous systems. Key factors such as pH,  $\text{H}_2\text{O}_2$  concentration, and catalyst type significantly influence the degradation efficiency, with an optimal pH range of 3–5 to maximize hydroxyl radical ( $\bullet\text{OH}$ ) generation. Metal oxide-based catalysts exhibit superior performance in radical production and  $\text{Fe}^{2+}$  regeneration. However, challenges remain in ensuring catalyst stability and optimizing large-scale application processes. Further research on catalyst design and reaction strategies is essential to enhance the practicality and sustainability of the heterogeneous Photo-Fenton process for industrial wastewater treatment.

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